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SPECTROSCOPIC STUDIES OF CARBON DISULFIDE AT HIGH
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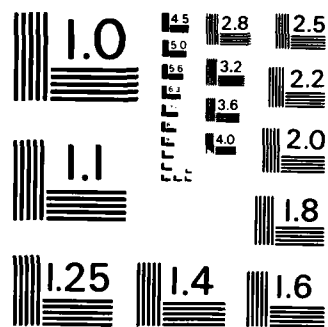
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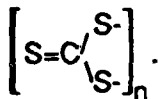
Spectroscopic Studies of Carbon Disulfide at High Pressure

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INTRODUCTION

Recent work on the transient absorption spectra induced by the dynamic shock-loading of carbon disulfide has shown¹ a shock-induced shift of the UV absorption edge up to a pressure of 8.0-9.0 GPa followed by irreversible chemistry in which the CS₂ becomes opaque. The authors suggested that this reaction was analogous to the Bridgman's Black polymer which has been observed to occur when CS₂ was heated to 185 C at 5.5 GPa², 250 C at 3.3 GPa³, or over a range of pressures and temperatures.⁴ The latter work on this reaction at static high pressure has shown⁴ infrared and visible/near-IR absorption spectra for the recovered CS₂ polymer and deduced that it was a mixture of carbon, sulfur, and an ill-defined polymer with the probable structure



While it is certainly reasonable that the irreversible chemistry observed in the shock studies is analogous to the irreversible chemistry which has been observed in the recovered static high pressure and high temperature studies, there has as yet been no direct spectroscopic link between the shock-induced and the static high pressure experiments. We wish to report the first such spectroscopic link for CS₂. In addition, there has been no measurement of the absorption edge shift of CS₂ at static high pressure and temperature similar to those of the shock experiments. We have used diamond-anvil cells and a combination of Raman, infrared, and UV-vis-NIR absorption spectroscopies to analyze the behavior of CS₂ in the pressure range 0.2-10.0 GPa and have compared one of these spectroscopic observables, the UV- absorption edge shift prior to the onset of irreversible chemistry, with that measured in the shock experiment.

EXPERIMENTAL

Merrill-Bassett diamond-anvil cells⁵ made of inconel 750 and equipped with type 2a diamonds were loaded with CS₂ purified by standard techniques, either neat or diluted with an appropriate amount of dichloromethane. Pressure was measured by means of the ruby fluorescence⁶, assuming the R₂ line shift to be 0.1322 GPa/cm⁻¹.

Raman spectra were obtained on a SPEX 1403 double monochromator by

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means of a back-scattering technique. Resolution was three cm^{-1} and typically ten or more spectra were signal averaged using a Nicolet 1180E Raman data system. Spectra-Physics model 171 Kr^+ laser was used at 647.1 nm with 35 mW. Infrared spectra were obtained with a Digilab FTS-20CV evacuable FTIR equipped with specially designed condensing optics and a liquid N_2 cooled MCT detector. Typically, 100 scans were averaged at a resolution of 2 cm^{-1} . Absorption of the diamonds obscured the IR spectra over the range 1950-2250 cm^{-1} . Visible absorption spectra were recorded with a Perkin-Elmer 330 spectrometer equipped with a beam condensor and the model 2600 data station. Diamond absorption blocked wavelengths shorter than 230 nm.

A small heater was built which allowed UV-visible and pressure measurements up to 300 C. It consisted of an aluminum cylinder into which the cell was inserted and around which a nichrome heater was wound. Mica sheets provided electrical insulation for the heater wire from the aluminum and ceramic standoffs, which were turned from a machinable ceramic, provided thermal insulation from the mounts. The ruby fluorescence peak determined the pressure of the cell with the zero bar peak position adjusted for temperature.

RESULTS

The behavior of the phonons of neat CS_2 over the pressure range 1.8-8.3 GPa is shown in Fig. 1. The pressure dependence over the range 1.8-4.0 GPa agrees with that previously reported.⁷ As can be seen, the phonon modes march up in frequency as a function of pressure and show no evidence for any phase transitions. This behavior is only evident for carefully grown single crystals of a particular orientation. Figure 2 shows a series of spectra illustrating that the different crystal orientations evidently affect the relative intensities of the three phonon peaks quite severely. In addition, as the pressure is increased for multi-crystalline samples, severe pressure gradients develop in the cell as evidenced both by the variation of the ruby fluorescence peak as well as by differences in the frequencies of the phonon features, both as a function of position in the cell. This extreme anisotropy is unusual for the relatively low pressure range 3.0-8.0 GPa and suggests that crystalline CS_2 is highly anisotropic at these pressures. This is equivalent to saying that the elastic constants vary along different crystallographic directions.

We also note that CS_2 becomes extremely photosensitive at pressures in excess of 4.0 GPa. However, it is possible to use red radiation of a low power level (647.1 nm, <30 mW) to obtain Raman spectra up until the point of pressure-induced chemistry, ca. 8.3 GPa. We found that neat CS_2 undergoes pressure-induced chemistry at or above this pressure which results in a solid that appears dark red when pressure is released to one bar. The absorption edge red-shifts markedly with increasing pressure, becoming opaque at pressures greater than 5.0 GPa. Partially reacted samples at 8.3 GPa show an inhomogeneous red color distribution throughout the now yellowish CS_2 , the infrared spectrum of which is shown in Fig. 3b. The features at 1074 and 1150 cm^{-1} correspond to previously measured³ peaks characteristic of the Bridgman's Black polymer. Our material is not black, however, and is rather intensely red as is evident in either partially reacted samples or in thin layers of the recovered product as measured between diamond anvils without a gasket. The infrared spectrum in Fig. 3c is of such a thin layer of the CS_2 reaction product and also shows the two features mentioned above. Thus it seems rather clear that this pressure-induced reaction of CS_2 is producing a similar if not identical product (or products) to that produced at lower pressure but higher temperature (5.5 GPa and 185 C or 3.3 GPa and 250 C). The visible-NIR absorption of a thin layer of the recovered product isolated between two diamond anvils without a gasket is shown in Fig. 4a. This spectrum differs substantially from that measured⁴ previously for the high temperature, high pressure reaction product, despite the fact that the infrared features measured on this product match ours very well. Whereas we have found a band edge that peaks at 22,500 cm^{-1} and is centered at 17,500 cm^{-1} , Chan and Jonscher measured⁴ two features at 13,710 and 9678 cm^{-1} . It is not yet clear why their spectrum differs from



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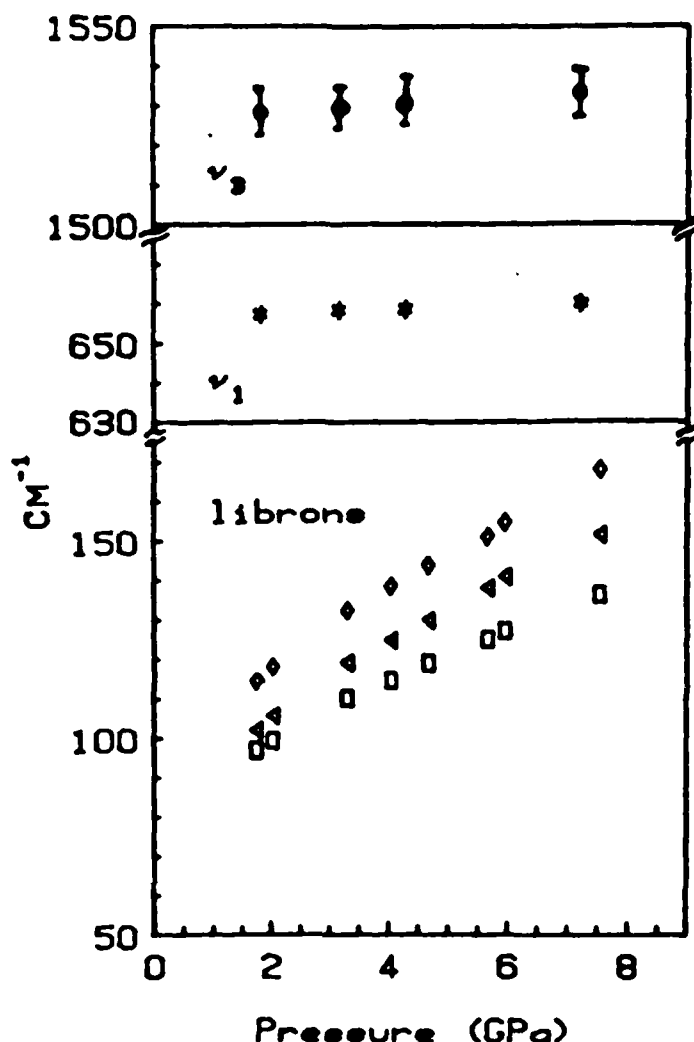


Fig. 1. Pressure dependence of librins and internal modes, ν_1 and ν_3 , for CS_2 .

ours. The spectrum in Fig. 4b is of a thin layer of the recovered product from our 2.4 GPa and 200 C reaction and shows a broad feature at $14,500 \text{ cm}^{-1}$. We believe that the dependence of this absorption feature on reaction conditions indicates a variation in the product distribution and/or polymer chain length. This question will be addressed further in a future publication.

The shift in the absorption edge of CS_2 as a function of pressure at ambient temperature is shown in Fig. 5 along with the results of Ogilvie and Duvall.¹ These latter results were obtained during shock-loading CS_2 with either step or ramp shocks. As can be seen, the results of the static measurements overlay those obtained from the ramp shock loading exactly, indicating that the ramp wave does indeed represent an isothermal compression in the thin cell ($\sim 1 \mu$), as was suggested by the authors. The results from step shock loading experiments shown in Fig. 5 differ substantially from those of the other two measurements. This difference can be explained, however, solely on the basis of the temperature induced shift of this same absorption edge. We have measured the absorption edge at 2.4 GPa for 28, 103, and 150 C as 366.1, 371.6, and 380.0 nm, respectively. On the basis of these temperature induced shifts at 2.4 GPa, we estimate the temperature of the step shock loaded CS_2 to be 218 C at 2.4 GPa, as compared to 353 C derived⁷ from Sheffield and Duvall's equation-of-state. A peak appeared at $22,700 \text{ cm}^{-1}$ for the 150 C measurement, evidently due to the accumulation of a product species induced in the still solid phase of CS_2 . The CS_2 became very photosensitive at this point and even the 647.1 nm laser irradiation

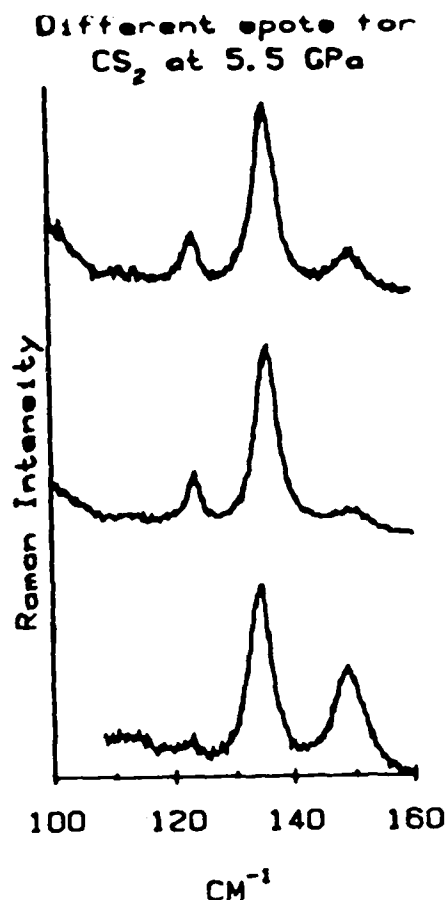


Fig. 2. Libron spectra of CS_2 for different crystal orientations.

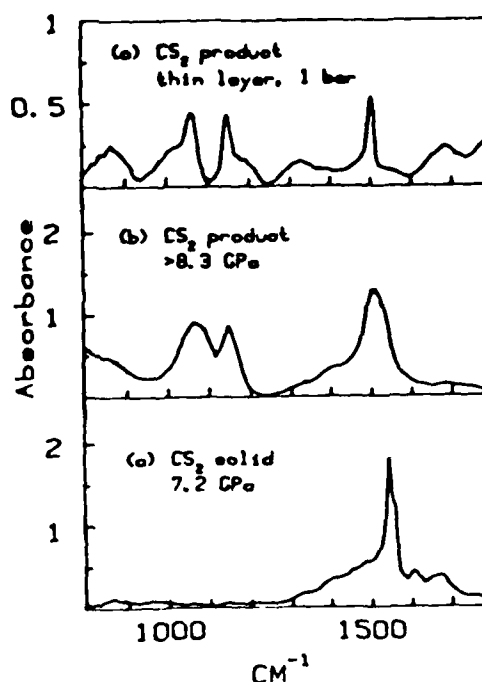


Fig. 3. Infrared spectra of: (a) single crystal CS_2 $33\ \mu$ thick at 7.2 GPa; (b) Reacted sample at >8.3 GPa; (c) thin layer of product at one bar. Note that interference fringes underlie the product bands.

produced sample decomposition as noted by the appearance of a black spot in the sample. The melting point was reached at 181 ± 6 C and although a ruby pressure measurement was not possible due to sample photosensitivity, we feel that the pressure was 2.4 ± 0.2 GPa based upon the temperature-induced pressure shift up until that point. The temperature was raised to 200 C and, during the course of a scan (ca. 10 minutes), the sample had reacted completely, this time forming a black solid with various infrared and visible-NIR features indicating that this product was the same as that measured previously and known as Bridgeman's Black.

Figure 1. shows the shift of the symmetric and the antisymmetric stretches (ν_1 and ν_3) for neat CS_2 . The pressure-induced shifts of both these bands are quite small. The Raman band shifts $2.6\ \text{cm}^{-1}$, 657.4 to $660.0\ \text{cm}^{-1}$, over the range 1.8 to 7.2 GPa ($0.48\ \text{cm}^{-1}/\text{GPa}$) and, we estimate that ν_3 shifts at about $1.3\ \text{cm}^{-1}/\text{GPa}$, although the width of this feature (ca. $20\ \text{cm}^{-1}$) made the determination somewhat difficult. If the CS_2 is diluted with dichloromethane (CH_2Cl_2), however, the infrared band (Fig. 6) moves substantially, $30\ \text{cm}^{-1}$ over the range 2.4 to 10.4 GPa ($3.75\ \text{cm}^{-1}/\text{GPa}$).

Unfortunately, it was not possible to obtain the complimentary Raman band positions due to the low concentration (around 1%) needed to put the infrared feature on scale. At these concentrations, there was no reaction of the CS_2 either with itself or with the dichloromethane up to the highest pressure that was possible

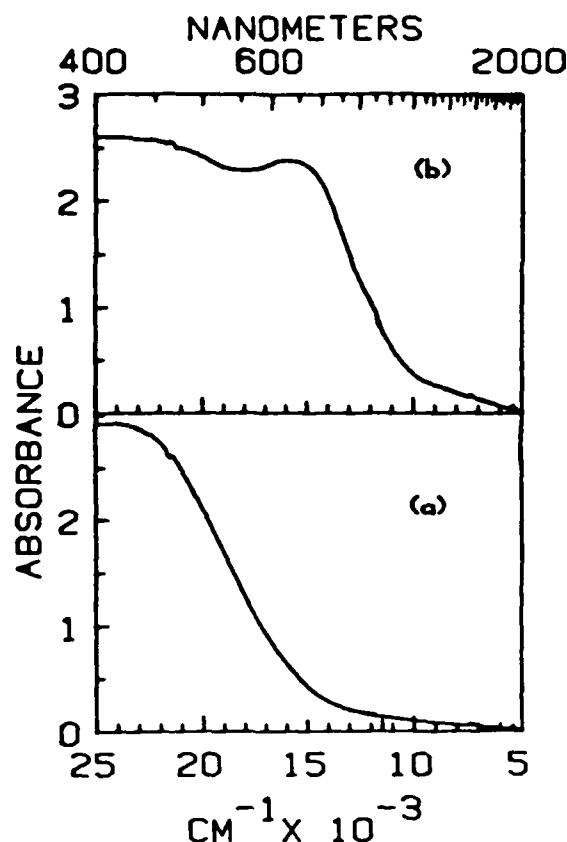


Fig. 4. Visible-NIR absorption of CS_2 product in thin layers at one bar. a) Reaction product from 8.3 GPa and ambient temperature. b) Reaction product from 2.4 GPa and 200 C.

with the cell used, 10.4 GPa. The UV absorption feature also red shifts significantly over the same pressure range, although the red-shifting tail of the dichloromethane obscured the exact band position of the CS_2 at pressures over 4.0 GPa.

We note that with concentrations higher than 10% CS_2 , a brown color appeared upon solidification of the solution which reversed upon melting unless the frozen solution was subjected to either increasing pressure or excessive laser irradiation. The product of this irreversible chemistry showed infrared features identical to those mentioned above for the reaction of neat CS_2 , and no evidence for a solute solvent reaction was found.

DISCUSSION

Our results for the shift of the phonons and internal modes of CS_2 over the range 1.8 to 8.3 GPa agree with the more limited results reported⁷ by Shimizu and Ohnishi. However, they claimed that they could not obtain Raman data above 4.0 GPa due to sample decomposition. We have found, on the other hand, that with the 647.1 nm Kr^+ line at a low power, Raman spectra could be obtained up until the point of the pressure-induced chemistry at 8.3 GPa. It was not possible, though, to obtain spectra with either blue or green excitation above 4.0 GPa due to increased photochemical reactivity. Shimizu and Ohnishi further argued⁷ that the Raman-active symmetric stretch (ν_1) shifts very little with pressure because it is an internal mode, despite the fact that most internal modes shift far more than this over a similar pressure range. For instance, nitrogen shifts⁸ 6 cm^{-1} (2336 to 2342 cm^{-1}) over the range 2.4 to 4.8 GPa ($2.5 \text{ cm}^{-1} / \text{GPa}$), which is five times that of CS_2 over a

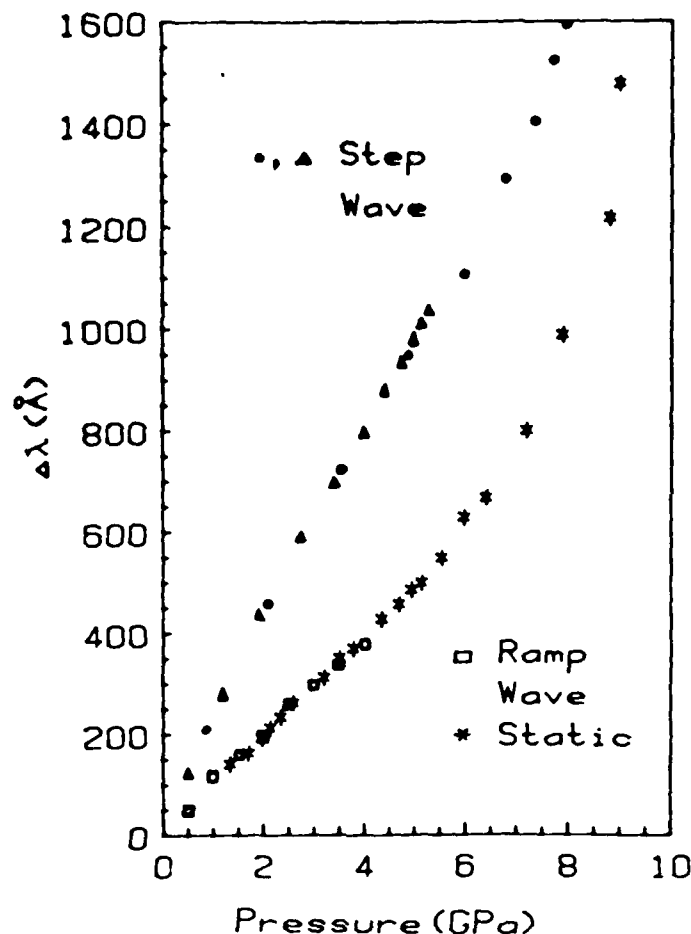


Fig. 5. Shift of absorption edge of CS_2 as a function of pressure for two step shocks (•, Δ) and an isothermal ramp shock (◻) from Duvall and coworkers¹ and for static high pressure at ambient temperature (*).

similar range. Nitrogen is stable to quite high pressure and the high frequency that results from its triple bond is representative of perhaps the prototypical isolated internal mode. It would, then, be quite surprising if CS_2 turned out to have a more isolated internal mode than nitrogen.

The classical interpretation of the pressure induced shifts of vibrational transitions begins with the partition of the vibrational hamiltonian as $H = H_0 + H_1 + \delta$ where $H_0 = f_{\text{har}} q^2 + f_{\text{anhar}} q^3$, H_1 is the bath, δ is the perturbation, and f_{har} and f_{anhar} are the harmonic and anharmonic force constants, respectively. A Taylor expansion of the perturbation along a normal coordinate followed by the application of first order perturbation theory results in the following expression for the frequency shift,

$$\Delta\nu = \nu_0 - \nu_{\text{gas}} = \frac{1}{\nu_{\text{gas}}} \left[-\frac{3f_{\text{anhar}}}{f_{\text{har}}} \left[\frac{\partial \delta}{\partial q} \right]_0 + \left[\frac{\partial^2 \delta}{\partial q^2} \right]_0 \right]$$

as per Benson and Drickamer.¹⁰ The four types of interactions considered to be most important are dispersive (induced dipole-induced dipole), inductive (dipole-induced dipole), dipolar (dipole-dipole), all of which are attractive, and the repulsive $1/R^{12}$. Since CS_2 has no permanent dipole, there is no dipolar interaction in the potential. The pressure range of this study suggests that we are in a regime where the repulsive interactions should dominate the attractive ones. Indeed, the

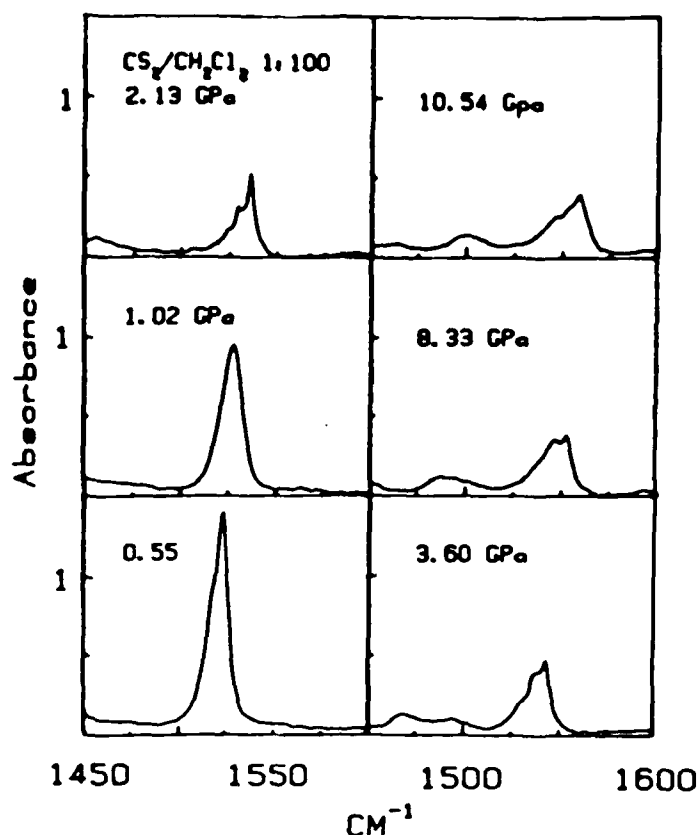


Fig. 6. Infrared spectra of $\text{CS}_2/\text{CH}_2\text{Cl}_2$ solutions at the pressures noted and ambient temperature.

fact that the splitting between ν_1 and ν_3 (the symmetric and antisymmetric stretches) is not pressure dependent implies that the inductive interactions are not varying appreciably with pressure, since ν_3 is dipole allowed in contrast to ν_1 and therefore affected more by the inductive interactions. Conversely, since the dispersive interactions depend on molecular polarizability, they should affect ν_1 more strongly than ν_3 . The repulsive interaction, on the other hand, should affect ν_1 and ν_3 in a similar way and therefore not influence the ν_1/ν_3 splitting. Note that the above mentioned model for the vibrational shift as a function of pressure has assumed that the intramolecular potential function remains pressure invariant, i.e., that f_{har} and f_{anhar} are pressure invariant. If there is an electronic interaction which mixes the groundstate wavefunctions of adjacent molecules, the intramolecular potential could then become pressure or density dependent which is exactly what we suggest is occurring in CS_2 .

Thus, we offer an alternative explanation for the small shift of ν_1 and ν_3 with pressure. It is that two competing effects, each driving the frequencies in opposite directions at nearly the same rate, cause the internal modes to shift up in frequency with increasing in pressure more slowly than is usual for internal modes that are subject to repulsive interactions. The first effect is due to decreasing intermolecular distances pushing the atoms of the molecules up against the repulsive wall of the stretching coordinates. This occurs, as we have stated above, when the repulsive intermolecular interactions predominate at high pressure and results in the frequency of the internal mode climbing with increasing pressure. The second, compensating effect is an electronic one involving an increasing overlap of the groundstate wavefunctions of adjacent molecules. The formation of this "extended bond" results in a decrease in the force constant of the internal modes which are sensitive to this change. Thus, while increasing intermolecular repulsion increases

the frequency of the internal mode as per the equation shown above, the mixing of groundstate wavefunctions serves to decrease f_{har} and f_{anhar} thus decreasing the frequency. A similar situation has been noted¹¹ with H_2 where the internal mode first increases, then flattens out, subsequently decreasing as pressure increases. Oxygen at high pressure also shows¹² similar behavior in its α phase. Here the Raman-active stretch increases with increasing pressure while the infrared-active stretch decreases at twice the rate. Therefore, the authors argued that the oxygen's bond strength is actually decreasing with increasing pressure.

The ambient temperature pressure-induced chemistry at 8.3 GPa could very well result from the completion of the intermolecular overlap which we used to explain the insensitivity of the vibrational modes with pressure. The product is similar with that obtained⁴ at lower pressure and higher temperature (3.3 GPa and 250 C). We have no evidence for either graphite or elemental sulfur as was found⁴ in the harsher temperature, milder pressure CS_2 reaction, although we cannot entirely rule it out since our spectroscopic methods are not sensitive to either of these species (provided that the sulfur is amorphous). We believe, however, that the milder conditions of our ambient temperature study would not permit this more severe redox chemistry and that only the more simple addition chemistry takes place in this case. In support of this hypothesis is the fact that our visible/NIR absorption (Fig. 4a) for the ambient temperature pressure-induced reaction does differ from that reported earlier for the recovered CS_2 product. Dilution studies with dichloromethane also support this notion, since any environment that produces graphite and sulfur would most likely also produce a solvent reaction. However, we have observed no such reaction with dichloromethane as the solvent at ambient temperature. It is reasonable to assume, then, that this reaction of CS_2 is a concerted one and involves many CS_2 moieties leading to the proposed Bridgman's Black structure as shown in the introduction.

The shift of the uv absorption edge as a function of static high pressure matches that obtained by means of an isothermal ramp shock exactly which means that the ramp shock is producing an isothermal compression and that the CS_2 is solid during the ramp shock as it is in our static high pressure measurement. A more surprising and unexpected similarity occurs between the step shock experiment and our static high pressure work. That is, while Duvall and Ogilvie noted¹ the onset of irreversible chemistry when their shock strength produced a pressure in the CS_2 in excess of 8.6 GPa and 600 C, we find that pressure-induced irreversible chemistry takes place in the solid at 8.3 GPa and ambient temperature. Although the similarity in the pressure dependence of the uv absorption edge between the isothermal ramp shock and the static high pressure experiment is not too surprising, the very similar pressures for the onset of irreversible chemistry in CS_2 between the static high pressure and the step shock experiments is very puzzling in that the temperatures are so very different. It is known, for instance, that increasing the temperature lowers⁴ the pressure threshold for the CS_2 reaction markedly. For instance, as noted above, at 250 C, the reaction proceeds at 3.3 GPa. Indeed, we have found that the reaction occurs on a several minute time scale at 2.4 GPa and 200 C. The only possible way that we have to explain the similar pressures for the onset of irreversible chemistry between the step shock and the static high pressure work on CS_2 is for there to be a strong kinetic factor for the chemistry at high pressure. That is, since the step shock experiment takes the CS_2 up in both temperature and pressure over a very short time scale, a small rate constant for the subsequent reaction (i.e., a high activation barrier) could prevent the subsequent reaction from occurring until some limiting threshold was reached. The rate of the step-shock induced reaction has been observed¹ to accelerate dramatically with increasing pressure over the 8.6 GPa threshold, which is consistent with our kinetic argument. Our much lower predicted temperature (218 versus 353 C) for the step shock at 2.4 GPa could be used to calibrate the Sheffield EOS. This difference in temperature might indicate that thermal equilibrium had not yet been achieved in the sample were it not for the fact that Duvall, et al., performed an isentropic ramp shock measurement with a thick cell of CS_2 . The shift of the absorption edge for this experiment followed the step shock curve, although the time scales for the two experiments are much different.

The dilution studies are also useful in isolating the two counteracting effects

for neat CS_2 . Thus, in dichloromethane the electronic interaction is effectively eliminated due to CH_2Cl_2 's much higher electronic states as well as its very different electronic character. There is a substantial shift to higher frequency for ν_3 , the infrared active C-S stretch, with increasing pressure, which indicates that repulsive intermolecular interactions dominate over the attractive dispersive and inductive forces, the latter due to the solvent polarity. At higher concentrations than 1%, the $\text{CS}_2 / \text{CH}_2\text{Cl}_2$ turns brown reversibly when the solution solidifies at 2.5 GPa. The visible absorption spectrum does not show any distinct features, simply a tail underlying the UV band at 340 nm. There are no new infrared features accompanying this transformation either, although there was evidence for CS_2 in both the CH_2Cl_2 crystal as well as in agglomerates with itself in that different infrared features are discernable for these two environments, and further, laser illumination resulted in photodecomposition. We expect that the presence of the reversible color change that occurs in these more concentrated $\text{CS}_2 / \text{CH}_2\text{Cl}_2$ solutions upon solidification is due to the same electronic interactions we invoked above to explain both the onset of chemistry as well as the insensitivity of the internal modes to pressure.

In summary, we have identified the pressure for the onset of CS_2 chemistry at ambient temperature and have correlated it with the several other indicators of increasing electronic interaction. We have further explained the rather small shift of ν_1 and ν_3 with pressure as due to compensating effects of intermolecular repulsion and electronic ground-state mixing. Our measurement of the UV absorption edge with pressure matches that measured in an isothermal ramp shock and we have been able to estimate the temperature of a step shock at 2.4 GPa as well. There are further indications of various molecular and polymer species present as a result of our infrared work and the relative amounts of these species are affected by the temperature, pressure, and physical state of the CS_2 .

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ABSTRACT

The absorption-edge shift as a function of high pressure is reported for carbon disulfide for the range 1.8 to 8.3 GPa. The absorption edge shift compares favorably with the isothermal ramp-wave results of other workers. The absorption edge shift with temperature at 2.4 GPa was also measured and allows a prediction of the temperature of the step-shock experiments of 220 C versus 350 C predicted on the basis of previous EOS calculations. The libron modes show strong dependence on crystal orientation at high pressure and an irreversible polymerization is noted at 8.3 GPa. The CS₂ product shows some of the infrared characteristics of Bridgeman's Black, which has been formed at 185 C and 5.5 GPa. The rather small pressure-induced shift of ν_1 and ν_3 is explained on the basis of compensating effects involving intermolecular repulsive versus electronic overlap between adjacent CS₂'s.

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